ON THE TWO-POTENTIAL CONSTITUTIVE MODELLING OF RUBBER VISCOELASTIC MATERIALS

BY

ADITYA KUMAR

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Civil Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2016

Urbana, Illinois

Adviser:

Professor Oscar Lopez-Pamies

ABSTRACT

This work lays out the specialization of the two-potential constitutive framework — also known as the "generalized standard materials" framework — to rubber viscoelasticity. *Inter alia*, it is shown that a number of popular rubber viscoelasticity formulations, introduced over the years following different approaches, are special cases of this framework. As a first application of practical relevance, the framework is utilized to put forth a new objective and thermodynamically consistent rubber viscoelastic model for incompressible isotropic elastomers. The model accounts for the non-Gaussian elasticity of elastomers, as well as for the deformation-enhanced shear thinning of their viscous dissipation governed by reptation dynamics. The descriptive and predictive capabilities of the model are illustrated via comparisons with experimental data available from the literature for two commercially significant elastomers.

To my parents, for their endless love and support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

While within certain ranges of loading conditions elastomers may be safely idealized as elastic, they are intrinsically viscoelastic. In the literature, there are, in essence, two approaches that have been adopted to model their viscoelastic behavior at a continuum level. The first approach is grounded on hereditary integral representations of the stress (strain) in terms of the strain (stress) (see, e.g., [1–3]), whereas the second one is based on the employment of internal variables to describe their viscous dissipation (see, e.g., [4–9]). Because of its superior tractability, the internal-variables approach has proved overwhelmingly more popular. Now, within the theoretical description of dissipative (not just viscoelastic) phenomena based on internal variables [10], the so-called two-potential framework [11–14] — also known as the "generalized standard materials" framework — has emerged as a framework of choice to construct thermodynamically consistent models for a wide range of phenomena such as for instance plasticity [15], fracture [16], and ferroelectricity [17]. Yet, somewhat surprisingly, the specialization of this framework to the case of rubber viscoelasticity does not appear to have been reported in the literature.[1]

The purpose of this work is to lay out the two-potential constitutive framework for rubber viscoelasticity. The consistency of the framework with material frame indifference, material symmetry, and the second law of thermodynamics is placed on record. As an illustration of the generality of the framework, it is also shown that a number of popular rubber viscoelasticity formulations, which have been introduced over the years using different approaches, can all be derived from the two-potential constitutive framework.

A second objective of this work is to put forth, by means of the two-potential framework, a new objective and thermodynamically consistent viscoelastic model for the practically relevant case of isotropic incompressible elastomers. The model

[1] There are, however, a number of models in the literature that have been proposed using directly this approach (see, e.g., [18, 19]).

accounts for the non-Gaussian elasticity of elastomers, as well as for the deformation-enhanced shear thinning of their viscous dissipation governed by the reptational motion of the underlying polymer chains. The computational tractability and robustness of the model is illustrated together with its predictive and descriptive capabilities via comparisons with experimental data available from the literature for two commercially significant elastomers, Nitrile rubber and the acrylate elastomer VHB 4910 from 3M.

CHAPTER 2

THE TWO-POTENTIAL FRAMEWORK FOR RUBBER VISCOELASTICITY

The two-potential framework in mechanics The key idea behind the two-potential constitutive framework is to describe the manner in which a material stores and dissipates energy by means of two thermodynamic potentials: (*i*) a free energy function ψ and (*ii*) a dissipation potential ϕ. In the context of mechanics [11–14], formally,

$$\psi = \psi(\mathbf{F}, \Lambda) \qquad \text{and} \qquad \phi = \phi(\mathbf{F}, \Lambda, \dot{\Lambda}) \tag{2.1}$$

under isothermal conditions, where $\mathbf{F}$ is the deformation gradient tensor, Λ stands for a finite number of (macroscopically non-observable) internal variables, and $\dot{\Lambda} = \mathrm{d}\Lambda/\mathrm{d}t$ denotes the time derivative of Λ. Both of these potentials are required to be non-negative and objective functions. In addition, the dissipation potential ϕ is required to be convex in $\dot{\Lambda}$ and such that $\arg\min_{\dot{\Lambda}} \phi(\mathbf{F}, \Lambda, \dot{\Lambda}) = \mathbf{0}$. The constitutive relation implied by these potentials is given by the following two coupled equations:

$$\mathbf{S} = \frac{\partial \psi}{\partial \mathbf{F}}(\mathbf{F}, \Lambda), \qquad \frac{\partial \psi}{\partial \Lambda}(\mathbf{F}, \Lambda) + \frac{\partial \phi}{\partial \dot{\Lambda}}(\mathbf{F}, \Lambda, \dot{\Lambda}) = 0, \tag{2.2}$$

where $\mathbf{S}$ stands for the first Piola-Kirchoff stress tensor and the differential equation in time $(2.2)_2$ is commonly referred to as the evolution equation for the internal variables Λ. By virtue of the objectivity of ψ and ϕ and the convexity of ϕ in $\dot{\Lambda}$, the constitutive relation (2.2) satisfies the principle of material frame indifference and the second law of thermodynamics. Moreover, it satisfies automatically the balance of angular momentum $\mathbf{S}\mathbf{F}^T = \mathbf{F}\mathbf{S}^T$.

Rubber viscoelasticity The specialization of the above constitutive framework to rubber viscoelasticity, much like to any other type of dissipative phenomenon, amounts to selecting appropriate internal variables Λ and appropriate thermodynamic potentials ψ and ϕ. For rubber viscoelasticity, this selection must account for at least five features (two microscopic and three macroscopic in nature) that

have been well established experimentally about elastomers: (*i*) the storage of energy is primarily governed by changes in entropy of the underlying polymer network, (*ii*) the dissipation of energy is primarily governed by friction among neighboring polymer chains, (*iii*) when all forces are removed after an arbitrary loading path, elastomers creep to their original configuration, (*iv*) when subjected to relaxation and creep loading conditions, elastomers exhibit a transient response that then evolves into an equilibrium state of deformation and stress, and (*v*) when subjected to loading conditions of the same type but different loading rate, elastomers exhibit different responses.

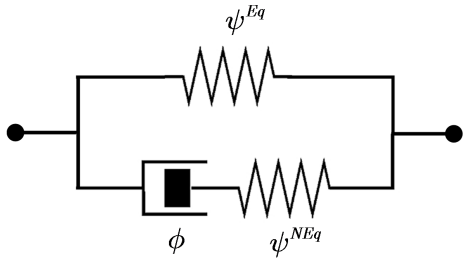


Figure 2.1: Rheological model of rubber viscoelastic behavior.

In the classical context of small-deformation linear viscoelastic behavior, features (*iii*) through (*v*) are encompassed by the basic rheological model depicted in Fig. 2.1. This model suggests that the internal variables Λ should be identified, loosely speaking, with a deformation gradient, $\mathbf{F}^v$ say, associated with the viscous (i.e., dissipative) part of the deformation, and moreover that

$$\psi = \psi^{Eq}(\mathbf{F}) + \psi^{NEq}(\mathbf{F}, \mathbf{F}^v) \qquad \text{and} \qquad \phi = \phi(\mathbf{F}, \mathbf{F}^v, \dot{\mathbf{F}}^v), \tag{2.3}$$

where the free energy function ψ^{Eq} serves to characterize the thermodynamic equilibrium states of the elastomer, while ψ^{NEq} serves to account for the additional energy storage at non-equilibrium states.

To proceed further, it is necessary to establish the precise definition of $\mathbf{F}_v$ and how the non-equilibrium part ψ^{NEq} of the free energy depends on it. Consistent with the rheological model depicted in Fig. 2.1 and motivated by earlier efforts [4], we take χ, the mapping between material points $\mathbf{X}$ in the undeformed reference configuration Ω_0 and their spatial position $\mathbf{x}$ in the deformed configuration Ω, to be given by the composition

$$\chi(\mathbf{X}) = \chi_e \circ \chi_v = \chi_e(\chi_v(\mathbf{X})) = \chi_e(\xi) \quad \text{with} \quad \xi = \chi_v(\mathbf{X}). \tag{2.4}$$

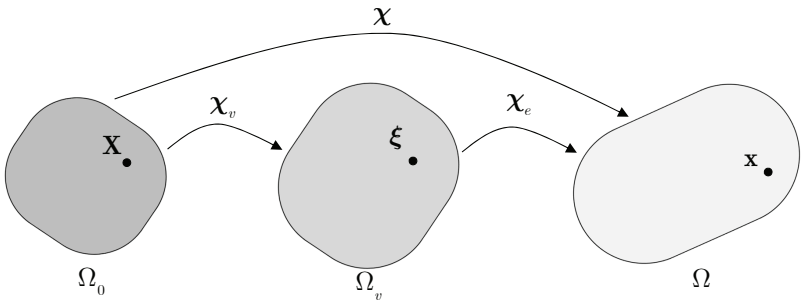


Figure 2.2: Schematic of the deformation field χ, mapping material points $\mathbf{X}$ in the undeformed reference configuration Ω_0 to their spatial position $\mathbf{x}$ in the current deformed configuration Ω, and its assumed composition (2.4).

Figure 2.2 shows a schematic of this composition. Granted the representation (2.4), it follows that

$$\mathbf{F} = \frac{\partial \chi}{\partial \mathbf{X}} = \frac{\partial \chi_e}{\partial \xi}\frac{\partial \chi_v}{\partial \mathbf{X}} = \mathbf{F}^e\mathbf{F}^v, \tag{2.5}$$

which defines $\mathbf{F}_v$. Here, it is important to emphasize that the composition (2.4) is a *constitutive assumption*. While other assumptions[1] that are consistent with the requirements of rubber viscoelasticity could be made leading to different definitions of $\mathbf{F}^v$, as it will become apparent below, the assumption (2.4) is amply general and yet convenient. Now, in view of relation (2.5) and motivated, again, by the rheological model in Fig. 2.1, we take that the dependence of ψ^{NEq} on $\mathbf{F}^v$ is only through $\mathbf{F}^e = \mathbf{F}\mathbf{F}^{v-1}$. With a slight abuse of notation we write $\psi^{NEq}(\mathbf{F},\mathbf{F}^{v-1}) = \psi^{NEq}(\mathbf{F}\mathbf{F}^{v-1}) = \psi^{NEq}(\mathbf{F}^e)$.

In short, under the physically based assumptions stated above, the free energy function ψ and dissipation potential ϕ in the general framework (2.1) specialize to

$$\psi = \psi^{Eq}(\mathbf{F}) + \psi^{NEq}(\mathbf{F}\mathbf{F}^{v-1}) \qquad \text{and} \qquad \phi = \phi(\mathbf{F},\mathbf{F}^v,\dot{\mathbf{F}}^v) \tag{2.6}$$

for rubber viscoelasticity. The implied constitutive relation (2.2) specializes in turn to

$$\begin{aligned} &\mathbf{S} = \frac{\partial \psi^{Eq}}{\partial \mathbf{F}}(\mathbf{F}) + \frac{\partial \psi^{NEq}}{\partial \mathbf{F}}(\mathbf{F}\mathbf{F}^{v-1}), \\ &\frac{\partial \psi^{NEq}}{\partial \mathbf{F}^v}(\mathbf{F}\mathbf{F}^{v-1}) + \frac{\partial \phi}{\partial \dot{\mathbf{F}}^v}(\mathbf{F},\mathbf{F}^v,\dot{\mathbf{F}}^v) = 0, \end{aligned} \tag{2.7}$$

[1]For instance, an alternative convenient choice could be to take the deformation field χ to be given by the composition $\chi(\mathbf{X}) = \chi'_v \circ \chi'_e$, where χ'_e stands for an "elastic" mapping while χ'_v stands for a "viscous" mapping. This assumption would lead to a deformation gradient $\mathbf{F}^v$ defined by $\mathbf{F} = \mathbf{F}^v\mathbf{F}^e$.

where, again, the internal variable $\mathbf{F}^v$ corresponds to the dissipative (viscous) part of the deformation as defined by (2.5).

2.0.1 Constraints on the functions ψ^{Eq}, ψ^{NEq}, ϕ

In the sequel, we spell out the constraints imposed on the functions ψ^{Eq}, ψ^{NEq}, ϕ in (2.6) by the principle of material frame indifference, material symmetry requirements, and the second law of thermodynamics.

Material frame indifference Under the generic change of observer $\mathbf{x}^* = \mathbf{Q}\mathbf{x} + \mathbf{c}$ with $\mathbf{Q} \in Orth^+$ and $\mathbf{c} \in \mathbb{R}^3$, it is required that the thermodynamic potentials ψ and ϕ in (2.6) remain invariant. A corollary of this condition is that the free energy function ψ^{Eq} must itself remain invariant for $\psi^{NEq} = 0$ at thermodynamic equilibrium states. Accordingly, noting that the deformation field χ_v is not connected to the deformed configuration Ω and hence changes in $\mathbf{x}$ do not have any effect on its gradient $\mathbf{F}^v$,

$$\begin{aligned} \psi^{Eq}(\mathbf{QF}) &= \psi^{Eq}(\mathbf{F}), \\ \psi^{NEq}(\mathbf{QF}\mathbf{F}^{v-1}) &= \psi^{NEq}(\mathbf{F}\mathbf{F}^{v-1}), \\ \phi(\mathbf{QF}, \mathbf{F}^v, \dot{\mathbf{F}}^v) &= \phi(\mathbf{F}, \mathbf{F}^v, \dot{\mathbf{F}}^v) \end{aligned} \tag{2.8}$$

for all $\mathbf{Q} \in Orth^+$ and arbitrary deformation gradients $\mathbf{F}$, $\mathbf{F}^v$. Here, it is worth remarking that the first two conditions in (2.8) imply balance of angular momentum $\mathbf{S}\mathbf{F}^T = \mathbf{F}\mathbf{S}^T$.

Material symmetry For elastomers with material symmetry group $Symm \subseteq Orth^+$, it is required that the thermodynamic potentials ψ and ϕ in (2.6) remain invariant under the change of reference configuration $\mathbf{X}^* = \mathbf{K}\mathbf{X}$ with $\mathbf{K} \in Symm$. Thus, upon recognizing that changes in the reference configuration Ω_0 involve changes in the deformation fields χ and χ_v,

$$\begin{aligned} \psi^{Eq}(\mathbf{FK}) &= \psi^{Eq}(\mathbf{F}), \\ \phi(\mathbf{FK}, \mathbf{F}^v\mathbf{K}, \dot{\mathbf{F}^v}\mathbf{K}) = \phi(\mathbf{FK}, \mathbf{F}^v\mathbf{K}, \dot{\mathbf{F}}^v\mathbf{K}) &= \phi(\mathbf{F}, \mathbf{F}^v, \dot{\mathbf{F}}^v) \end{aligned} \tag{2.9}$$

for all $\mathbf{K} \in Symm$ and arbitrary deformation gradients $\mathbf{F}$, $\mathbf{F}^v$. It is of note that material symmetry requirements impose *no* constraint on the free energy function

ψ^{NEq} since $\psi^{NEq}(\mathbf{F}\mathbf{K}(\mathbf{F}^v\mathbf{K})^{-1}) = \psi^{NEq}(\mathbf{F}\mathbf{K}\mathbf{K}^T\mathbf{F}^{v-1}) = \psi^{NEq}(\mathbf{F}\mathbf{F}^{v-1})$.

The second law of thermodynamics In the context of isothermal processes of interest in this work, the second law of thermodynamics imposes the following constraint on the dissipation potential ϕ in (2.6):

$$\left[\frac{\partial\phi}{\partial\dot{\mathbf{F}}^v}(\mathbf{F},\mathbf{F}^v,\dot{\mathbf{F}}^v)\right]\cdot\dot{\mathbf{F}}^v \geq 0 \tag{2.10}$$

for arbitrary deformation gradients $\mathbf{F}$, $\mathbf{F}^v$, with equality holding only when $\dot{\mathbf{F}}^v = \mathbf{0}$. Since, according to the two-potential framework, the function ϕ is non-negative, convex in $\dot{\mathbf{F}}^v$, and such that $\arg\min_{\dot{\mathbf{F}}^v}\phi(\mathbf{F},\mathbf{F}^v,\dot{\mathbf{F}}^v) = \mathbf{0}$, this inequality is automatically satisfied. A natural choice to comply with (2.10), which appears to be sufficiently general to model elastomers, is the quadratic functional form

$$\phi(\mathbf{F},\mathbf{F}^v,\dot{\mathbf{F}}^v) = \frac{1}{2}\dot{\mathbf{F}}^v\cdot\mathbf{A}(\mathbf{F},\mathbf{F}\mathbf{F}^{v-1})\dot{\mathbf{F}}^v, \tag{2.11}$$

where $\mathbf{A}$ is any positive-definite fourth-order tensor function of choice such that, in view of the requirements $(2.8)_3$ and $(2.9)_2$,
$A_{ijkl}(\mathbf{Q}\mathbf{F}\mathbf{K},\mathbf{Q}\mathbf{F}\mathbf{F}^{v-1}) = K_{mj}A_{imkn}(\mathbf{F},\mathbf{F}\mathbf{F}^{v-1})K_{nl}$ for all $\mathbf{Q}\in Orth^+$, $\mathbf{K}\in Symm$ and arbitrary $\mathbf{F}$, $\mathbf{F}^v$.

In the sequel, we shall restrict attention to dissipation potentials of the form (2.11). Instead of working directly with (2.11), however, we will work with the more convenient equivalent form

$$\phi(\mathbf{F},\mathbf{F}^v,\dot{\mathbf{F}}^v) = \frac{1}{2}\widetilde{\Gamma}^v\cdot\mathcal{A}(\mathbf{F},\mathbf{F}^e)\widetilde{\Gamma}^v, \tag{2.12}$$

where we recall that $\mathbf{F}^e = \mathbf{F}\mathbf{F}^{v-1}$ and have introduced the notation

$$\begin{aligned}
\widetilde{\Gamma}^v &= \mathbf{F}^e\Gamma^v\mathbf{F}^{e-1},\\
\Gamma^v &= \dot{\mathbf{F}}^v\mathbf{F}^{v-1},\\
\mathcal{A}_{ijkl}(\mathbf{F},\mathbf{F}^e) &= F^{e-1}_{mi}F_{jn}A_{mnrs}(\mathbf{F},\mathbf{F}\mathbf{F}^{v-1})F^{e-1}_{rk}F_{ls}.
\end{aligned} \tag{2.13}$$

By definition, $\mathcal{A}$ is any positive-definite fourth-order tensor function of choice such that

$$\mathcal{A}_{ijkl}(\mathbf{Q}\mathbf{F}\mathbf{K},\mathbf{Q}\mathbf{F}^e) = Q_{im}Q_{jn}Q_{kp}Q_{lq}\,\mathcal{A}_{mnpq}(\mathbf{F},\mathbf{F}^e) \tag{2.14}$$

for all $\mathbf{Q}\in Orth^+$, $\mathbf{K}\in Symm$ and arbitrary $\mathbf{F}$, $\mathbf{F}^e$.

In view of relation (2.12), the two potentials (2.6) and ensuing constitutive relation (2.7) for rubber viscoelasticity take the more explicit form

$$\begin{aligned}
&\psi = \psi^{Eq}(\mathbf{F}) + \psi^{NEq}(\mathbf{F}^e),\\
&\phi = \frac{1}{2}\mathbf{F}\mathbf{F}^{v-1}\dot{\mathbf{F}}^v\mathbf{F}^{-1}\cdot\left[\mathcal{A}(\mathbf{F},\mathbf{F}^e)\,\mathbf{F}\mathbf{F}^{v-1}\dot{\mathbf{F}}^v\mathbf{F}^{-1}\right],
\end{aligned} \tag{2.15}$$

and

$$\begin{aligned}
&\mathbf{S} = \mathbf{S}^{Eq} + \mathbf{S}^{NEq}\mathbf{F}^{v-T},\\
&\mathbf{S}^{NEq}\mathbf{F}^{v-T}\mathbf{F}^T - \mathcal{A}(\mathbf{F},\mathbf{F}^e)\,\mathbf{F}\mathbf{F}^{v-1}\dot{\mathbf{F}}^v\mathbf{F}^{-1} = \mathbf{0}.
\end{aligned} \tag{2.16}$$

Here, $\mathbf{S}^{Eq} = \partial\psi^{Eq}(\mathbf{F})/\partial\mathbf{F}$, $\mathbf{S}^{NEq} = \partial\psi^{NEq}(\mathbf{F}^e)/\partial\mathbf{F}^e$, and it is recalled again that $\mathbf{F}^e = \mathbf{F}\mathbf{F}^{v-1}$. For given choices of functions ψ^{Eq}, ψ^{NEq}, $\mathcal{A}$ subject to conditions $(2.8)_{1-2}$, $(2.9)_1$, (2.14) and given loading conditions, the evaluation of the stress-deformation response $(2.16)_1$ of the material requires the solution of the nonlinear first-order ordinary differential equation $(2.16)_2$ in time for the internal variable $\mathbf{F}^v$. For later reference, we remark that in terms of the Cauchy stress $\mathbf{T} = J^{-1}\mathbf{S}\mathbf{F}^T$, the constitutive relation (2.16) reads as

$$\mathbf{T} = \mathbf{T}^{Eq} + \frac{1}{J^v}\mathbf{T}^{NEq}, \qquad J^e\mathbf{T}^{NEq} - \mathcal{A}(\mathbf{F},\mathbf{F}^e)\,\mathbf{F}\mathbf{F}^{v-1}\dot{\mathbf{F}}^v\mathbf{F}^{-1} = \mathbf{0}, \tag{2.17}$$

where $J = \det\mathbf{F}$, $J^v = \det\mathbf{F}^v$, $J^e = \det\mathbf{F}^e$, $\mathbf{T}^{Eq} = J^{-1}\mathbf{S}^{Eq}\mathbf{F}^T$, $\mathbf{T}^{NEq} = J^{e-1}\mathbf{S}^{NEq}\mathbf{F}^{eT}$.

2.0.2 The case of isotropic materials

By and large, the types of elastomers of most practical interest in engineering applications are isotropic. In this subsection, we spell out the specialization of the constitutive framework (2.15)–(2.16) to such a class of materials.

The material symmetry group for isotropic elastomers is the entire proper orthogonal group and hence it follows from $(2.8)_{1-2}$, $(2.9)_1$ that

$$\psi^{Eq}(\mathbf{Q}\mathbf{F}\mathbf{K}) = \psi^{Eq}(\mathbf{F}), \qquad \psi^{NEq}(\mathbf{Q}\mathbf{F}^e) = \psi^{NEq}(\mathbf{F}^e) \tag{2.18}$$

for all $\mathbf{Q},\mathbf{K} \in Orth^+$ and arbitrary $\mathbf{F}$, $\mathbf{F}^e$. These conditions imply the following

expedient representations of ψ^{Eq} and ψ^{NEq}:

$$\psi^{Eq}(\mathbf{F}) = \widehat{\psi}^{Eq}(I_1, I_2, J), \qquad \psi^{NEq}(\mathbf{F}^e) = \widehat{\psi}^{NEq}(\mathbf{C}^e), \tag{2.19}$$

where $I_1 = \mathrm{tr}\mathbf{C}$, $I_2 = 1/2[(\mathrm{tr}\mathbf{C})^2 - \mathrm{tr}\mathbf{C}^2]$, $J = \sqrt{\det\mathbf{C}} = \det\mathbf{F}$ stand for the principal invariants of the right Cauchy-Green deformation tensor $\mathbf{C} = \mathbf{F}^T\mathbf{F}$, and $\mathbf{C}^e = \mathbf{F}^{eT}\mathbf{F}^e$. We remark that the free energy function ψ^{NEq}, as opposed to ψ^{Eq}, is *not* required to be an isotropic function.

Moreover, it follows from (2.14) that

$$\mathcal{A}_{ijkl}(\mathbf{QFK}, \mathbf{QF}^e) = Q_{im}Q_{jn}Q_{kp}Q_{lq}\mathcal{A}_{mnpq}(\mathbf{F}, \mathbf{F}^e) \tag{2.20}$$

for all $\mathbf{Q}, \mathbf{K} \in Orth^+$ and arbitrary $\mathbf{F}$, $\mathbf{F}^e$. A convenient, albeit incomplete, representation of $\mathcal{A}$ implied by this condition is given by

$$\begin{aligned}
\mathcal{A}_{ijkl}(\mathbf{F}, \mathbf{F}^e) \;=\; & 2\eta_K(I_1, I_2, J, \mathbf{C}^e, \mathbf{B}^v)\,\mathcal{K}_{ijkl} + \\
& 2\nu_K(I_1, I_2, J, \mathbf{C}^e, \mathbf{B}^v)F^{e\,-1}_{mi}F^e_{jn}\mathcal{K}_{mnpq}F^{e\,-1}_{pk}F^e_{lq} + \\
& 2\theta_K(I_1, I_2, J, \mathbf{C}^e, \mathbf{B}^v)\,\mathcal{K}_{ijmn}F^e_{mp}F^e_{lp}F^{e\,-1}_{qn}F^{e\,-1}_{qk} + \\
& 3\eta_J(I_1, I_2, J, \mathbf{C}^e, \mathbf{B}^v)\,\mathcal{J}_{ijkl}.
\end{aligned} \tag{2.21}$$

Here, $\mathbf{B}^v = \mathbf{F}^v\mathbf{F}^{v\,T} = \mathbf{F}^{e\,-1}\mathbf{B}\mathbf{F}^{e\,-T}$ with $\mathbf{B} = \mathbf{F}\mathbf{F}^T$ denoting the left Cauchy-Green deformation tensor, $\mathcal{K}$ and $\mathcal{J}$ stand for the orthogonal projections tensors

$$\mathcal{K}_{ijkl} = \frac{1}{2}\left[\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}\right], \qquad \mathcal{J}_{ijkl} = \frac{1}{3}\delta_{ij}\delta_{kl}, \tag{2.22}$$

where δ_{ij} denotes the Kronecker delta, and η_K, ν_K, θ_K, η_J are non-negative functions of their arguments. We recall that the projection tensors $\mathcal{K}$, $\mathcal{J}$ are such that $\mathcal{K}\mathcal{K} = \mathcal{K}$, $\mathcal{J}\mathcal{J} = \mathcal{J}$, and $\mathcal{K}\mathcal{J} = \mathcal{J}\mathcal{K} = \mathbf{0}$. We also emphasize that the functions η_K, ν_K, θ_K, η_J are *not* constrained to be isotropic functions of $\mathbf{C}^e$ or $\mathbf{B}^v$, namely, they are *not* constrained to depend on $\mathbf{C}^e$ or $\mathbf{B}^v$ only through their principal invariants $I^e_1 = \mathrm{tr}\mathbf{C}^e$, $I^e_2 = 1/2[(\mathrm{tr}\mathbf{C}^e)^2 - \mathrm{tr}\mathbf{C}^{e\,2}]$, $J^e = \sqrt{\det\mathbf{C}^e} = \det\mathbf{F}^e$, $I^v_1 = \mathrm{tr}\mathbf{B}^v$, $I^v_2 = 1/2[(\mathrm{tr}\mathbf{B}^v)^2 - \mathrm{tr}\mathbf{B}^{v\,2}]$, $J^v = \sqrt{\det\mathbf{B}^v} = \det\mathbf{F}^v$. For later reference, we note that the invariants I^e_1, I^e_2, J^e can be written in terms of the right Cauchy-Green deformation tensors $\mathbf{C}$ and $\mathbf{C}^v = \mathbf{F}^{v\,T}\mathbf{F}^v$ as follows: $I^e_1 = \mathrm{tr}(\mathbf{C}\mathbf{C}^{v\,-1}) = \mathbf{C}\cdot\mathbf{C}^{v\,-1}$, $I^e_2 = 1/2[(\mathrm{tr}(\mathbf{C}\mathbf{C}^{v\,-1}))^2 - \mathrm{tr}(\mathbf{C}^{v\,-1}\mathbf{C}\mathbf{C}^{v\,-1}\mathbf{C})] = 1/2[(\mathbf{C}\cdot\mathbf{C}^{v\,-1})^2 - \mathbf{C}^{v\,-1}\mathbf{C}\cdot\mathbf{C}\mathbf{C}^{v\,-1}]$, $J^e = \sqrt{\det\mathbf{C}/\det\mathbf{C}^v}$.

2.0.3 Connection with existing formulations

The two-potential constitutive framework defined by relations (2.15)–(2.16) is fairly simple, as its computational cost amounts to solving a nonlinear first-order ordinary differential equation for a second-order tensor, and yet admittedly general, as it applies to elastomers of arbitrary compressibility and anisotropy. Moreover, many of the formulations of rubber viscoelasticity that have been proposed in the literature over the years happen to be special cases of (2.15)–(2.16). In this subsection, for illustration purposes, we discuss three such formulations: the formulation of Le Tallec et al. [5], that of Reese and Govindjee [6], and the model of Bergström and Boyce [7].

The formulation of Le Tallec et al Le Tallec et al. [5] proposed a formulation for rubber viscoelasticity applicable to incompressible materials with general classes of anisotropy. In its general form, their formulation can be written out as a special case of the two-potential framework (2.15)–(2.16). More specifically, in the present notation, their formulation corresponds to setting

$$\psi^{Eq}(\mathbf{F}) = \begin{cases} \widehat{\psi}^{Eq}(\mathbf{C}) & \text{if} \quad J=1 \\ +\infty & \text{otherwise} \end{cases}, \qquad \psi^{NEq}(\mathbf{F}^e) = \begin{cases} \widehat{\psi}^{NEq}(\mathbf{C}^e) & \text{if} \quad J^e=1 \\ +\infty & \text{otherwise} \end{cases} \tag{2.23}$$

in the free energy function $(2.15)_1$ and

$$\mathcal{A}_{ijkl}(\mathbf{F},\mathbf{F}^e) = 2f_1 F^{e\,-1}_{mi} F^e_{jn} \mathcal{K}_{mnpq} F^{e\,-1}_{pk} F^e_{lq} + 3f_2 \mathcal{I}_{ijkl} \tag{2.24}$$

with constants $f_1 > 0$ and $f_2 = +\infty$ in the dissipation potential $(2.15)_2$. The unbounded value of f_2 in (2.24) implies that $\det \mathbf{F}^v = 1$.

The formulation of Reese and Govindjee In a subsequent effort, Reese and Govindjee [6] proposed a similar formulation for rubber viscoelasticity applicable to compressible materials with a restricted class of anisotropies. Save for a caveat, in its general form, this formulation too corresponds to a special case of the two-potential framework (2.15)–(2.16). Specifically, their formulation corresponds to setting

$$\psi^{Eq}(\mathbf{F}) = \widehat{\psi}^{Eq}(\mathbf{C}), \qquad \psi^{NEq}(\mathbf{F}^e) = \widehat{\psi}^{NEq}(\mathbf{C}^e) \tag{2.25}$$

in the free energy function $(2.15)_1$ and

$$\mathcal{A}_{ijkl}(\mathbf{F},\mathbf{F}^e) = g_1\left[\mathcal{K}_{ijkl} + \mathcal{K}_{ijmn}F^e_{mp}F^e_{lp}F^{e\,-1}_{qn}F^{e\,-1}_{qk}\right] + 3g_2\mathcal{J}_{ijkl} \tag{2.26}$$

with constants $g_1 > 0$, $g_2 > 0$ in the dissipation potential $(2.15)_2$. The caveat is that the general formulation — but not the numerical examples — of Reese and Govindjee [6] assumes the coefficients g_1 and g_2 in (2.26) to be functions of the left Cauchy-Green deformation tensor $\mathbf{B}^e = \mathbf{F}^e\mathbf{F}^{eT}$ and not just positive constants. This assumption violates the principle of material frame indifference as it can be readily deduced from condition (2.14). This significant drawback does not appear to have been realized in the literature until now.

The model of Bergström and Boyce Bergström and Boyce [7] proposed a model for compressible isotropic rubber viscoelastic materials, which, similar to the two earlier formulations discussed above, corresponds to a special case of the two-potential framework (2.15)–(2.16). Indeed, their model corresponds to setting

$$\psi^{Eq}(\mathbf{F}) = \widehat{\psi}^{AB}(I_1, J), \qquad \psi^{NEq}(\mathbf{F}^e) = \widehat{\psi}^{AB}(I^e_1, J^e) \tag{2.27}$$

in the free energy function $(2.15)_1$ and

$$\mathcal{A}_{ijkl}(\mathbf{F},\mathbf{F}^e) = 2h_1(I^e_1, I^e_2, J^e, I^v_1)\,\mathcal{K}_{ijkl} + 3h_2\mathcal{J}_{ijkl} \tag{2.28}$$

in the dissipation potential $(2.15)_2$. In these expressions, $\widehat{\psi}^{AB}$ denotes the stored-energy function of a compressible Arruda-Boyce material [20],

$$h_1(I^e_1, I^e_2, J^e, I^v_1) = \frac{J^e\left(J^{NEq}_2\right)^{\frac{1-m}{2}}}{C_1\left(\sqrt{\dfrac{I^v_1}{3}} - 1\right)^{C_2}}$$

$$\text{with} \quad J^{NEq}_2 = \frac{4}{J^{e\,2}}\left(\frac{I^{e\,2}_1}{3} - I^e_2\right)\left[\frac{\partial\widehat{\psi}^{AB}}{\partial I^e_1}(I^e_1, J^e)\right]^2, \tag{2.29}$$

and

$$h_2 = +\infty, \tag{2.30}$$

where $C_1 > 0$, $C_2 \in [0, -1]$, $m > 0$ are material constants and the notation $J^{NEq}_2 = 1/2\,\mathrm{dev}\mathbf{T}^{NEq} \cdot \mathrm{dev}\mathbf{T}^{NEq}$ has been introduced to denote the second invariant of

the stress deviator $\mathrm{dev}\mathbf{T}^{NEq} = \mathbf{T}^{NEq} - 1/3\,\mathrm{tr}\mathbf{T}^{NEq}\mathbf{I}$. We remark that the fourth-order tensor (2.28) characterizing the dissipation potential $(2.15)_2$ is a special case of the representation (2.21) corresponding to the choice $\eta_K(I_1, I_2, J, \mathbf{C}^e, \mathbf{B}^v) = h_1(I_1^e, I_2^e, J^e, I_1^v)$, $\eta_J(I_1, I_2, J, \mathbf{C}^e, \mathbf{B}^v) = h_2 = +\infty$, $\nu_K(I_1, I_2, J, \mathbf{C}^e, \mathbf{B}^v) = \theta_K(I_1, I_2, J, \mathbf{C}^e, \mathbf{B}^v) = 0$. The unbounded value of h_2 in (2.28) implies that $\det\mathbf{F}^v = 1$.

CHAPTER 3

PROPOSED MODEL FOR ISOTROPIC INCOMPRESSIBLE ELASTOMERS

In this section, we make use of the two-potential constitutive framework (2.15)–(2.16) to construct a new objective and thermodynamically consistent model for the rubber viscoelastic response of isotropic incompressible elastomers that: (*i*) satisfies the five microscopic and macroscopic features about elastomers outlined at the beginning of Section 2, (*ii*) is mathematically simple and amenable to numerical implementation for solving boundary-value problems, (*iii*) contains material parameters which may be given a physical interpretation, and, more importantly, (*iv*) is able to describe and predict the mechanical behavior of elastomers over wide ranges of deformations and deformation rates.

We begin by characterizing the equilibrium and non-equilibrium free energy functions in $(2.15)_1$ with the I_1-based stored-energy functions recently proposed by Lopez-Pamies [21]:

$$\psi^{Eq}(\mathbf{F}) = \begin{cases} \dfrac{3^{1-\alpha_1}}{2\alpha_1}\mu_1\left[I_1^{\alpha_1}-3^{\alpha_1}\right]+\dfrac{3^{1-\alpha_2}}{2\alpha_2}\mu_2\left[I_1^{\alpha_2}-3^{\alpha_2}\right] & \text{if} \quad J=1 \\ +\infty & \text{otherwise} \end{cases}, \tag{3.1}$$

$$\psi^{NEq}(\mathbf{F}^e) = \begin{cases} \dfrac{3^{1-a_1}}{2a_1}m_1\left[I_1^{ea_1}-3^{a_1}\right]+\dfrac{3^{1-a_2}}{2a_2}m_2\left[I_1^{ea_2}-3^{a_2}\right] & \text{if} \quad J^e=1 \\ +\infty & \text{otherwise} \end{cases}. \tag{3.2}$$

In these expressions, μ_r, α_r, m_r, a_r $(r=1,2)$ are real-valued material parameters[1] that may be associated with the non-Gaussian statistical distribution of the underlying polymer chains. In addition to its mathematical simplicity and physical meaning of its parameters, we choose this class of stored-energy functions because of its rich functional form and demonstrated descriptive and predictive capabilities

[1]The values of the parameters μ_r, α_r, m_r, a_r should be selected so that the stored-energy functions (3.1) and (3.2) are strongly elliptic. Simple sufficient conditions for strong ellipticity are given by $\mu_r > 0$, $\alpha_r > 1/2$, $m_r > 0$, $a_r > 1/2$ $(r=1,2)$. Sufficient and necessary conditions are given by relations (22) in [21].

to model the nonlinear elastic response of a broad variety of elastomers [21].

Molecular analyses [22–24] as well as macroscopic experiments [25–28] have by now established that elastomers exhibit *deformation-enhanced shear thinning*. In the context of the formulation (2.15)–(2.16) specialized to isotropic elastomers, this implies that the "viscosities" η_K, ν_K, and/or θ_K in the representation (2.21) of $\mathcal{A}$ are *not* constants (as in the formulations (2.24) and (2.26) of Le Tallec et al. and of Reese and Govindjee), but increasing functions of the applied deformation and decreasing functions of the deformation rate. In light of these requirements, we propose to make use of the following fourth-order tensor $\mathcal{A}$ in the dissipation potential $(2.15)_2$:

$$\mathcal{A}_{ijkl}(\mathbf{F},\mathbf{F}^e) = \eta_K(I_1^e, I_2^e, I_1^v)\left[\mathcal{K}_{ijkl} + \mathcal{K}_{ijmn}F^e_{mp}F^e_{lp}F^{e\,-1}_{qn}F^{e\,-1}_{qk}\right] + 3\eta_J\mathcal{J}_{ijkl}, \quad (3.3)$$

where

$$\eta_K(I_1^e, I_2^e, I_1^v) = \eta_\infty + \frac{\eta_0 - \eta_\infty + K_1\left[I_1^{v\beta_1} - 3^{\beta_1}\right]}{1 + \left(K_2 J_2^{NEq}\right)^{\beta_2}}$$

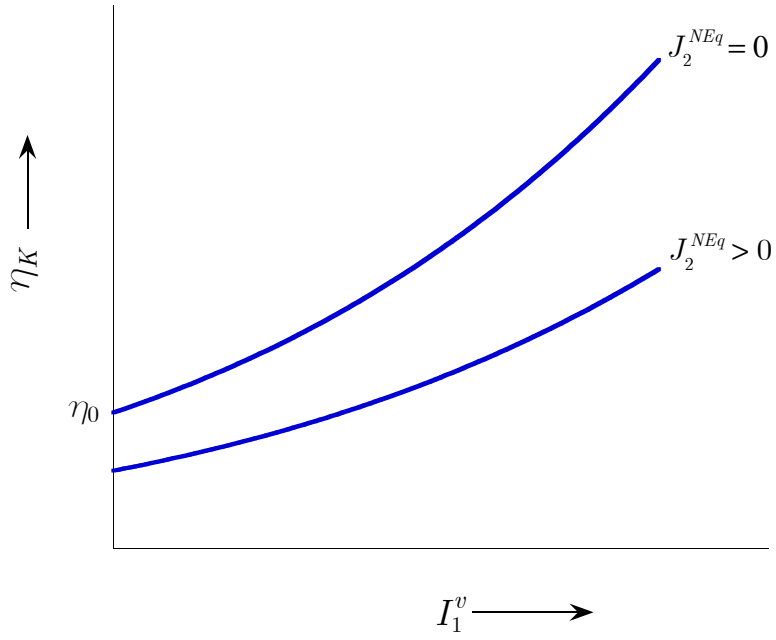
$$\text{with} \quad J_2^{NEq} = \left(\frac{I_1^{e\,2}}{3} - I_2^e\right)\left(\sum_{r=1}^{2} 3^{1-a_r} m_r I_1^{e\,a_r - 1}\right)^2 \quad (3.4)$$

and

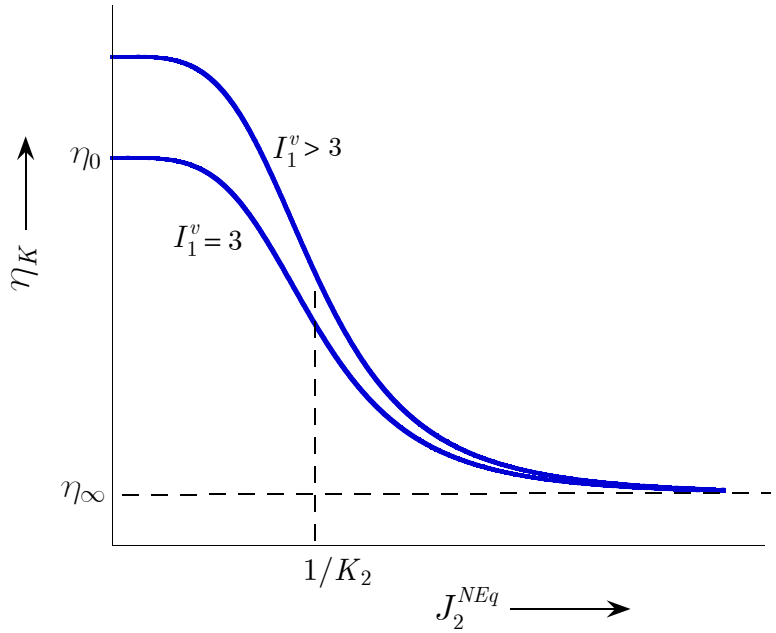
$$\eta_J = +\infty. \quad (3.5)$$

In expressions (3.4), $\eta_0 > \eta_\infty \geq 0$, $\beta_1 \geq 0$, $\beta_2 \geq 0$, $K_1 \geq 0$, $K_2 \geq 0$ are real-valued material parameters that may be associated with reptation dynamics and it is recalled that $J_2^{NEq} = 1/2\,\mathrm{dev}\mathbf{T}^{NEq}\cdot\mathrm{dev}\mathbf{T}^{NEq}$ stands for the second invariant of the stress deviator $\mathrm{dev}\mathbf{T}^{NEq} = \mathbf{T}^{NEq} - 1/3\,\mathrm{tr}\mathbf{T}^{NEq}$. As illustrated schematically by Fig. 3.1, the viscosity function η_K in (3.3) is an increasing function of I_1^v (and hence an increasing function of the applied deformation since I_1^v is proportional to $\mathbf{F}$) and a decreasing function of J_2^{NEq} (and hence a decreasing function of the deformation rate since $\mathbf{T}^{NEq}$ is proportional to $\dot{\mathbf{F}}$).

Having defined the free energy function $(2.15)_1$ with (3.1)–(3.2) and dissipation potential $(2.15)_2$ with (3.3)–(3.5), it is now a simple matter to spell out the constitutive relation (2.16) that they imply. Thus, the stress-deformation response $(2.16)_1$ is given by



(a)



(b)

Figure 3.1: Schematic of the deformation-enhanced shear thinning behavior of the proposed constitutive model: parts (a) and (b) illustrate how the viscosity function η_K increases with applied deformation (as measured by I_1^v) and decreases with deformation rate (as measured by J_2^{NEq}).

$$\mathbf{S} = \left[\sum_{r=1}^{2} 3^{1-\alpha_r}\mu_r I_1^{\alpha_r - 1}\right]\mathbf{F} + \left[\sum_{r=1}^{2} 3^{1-a_r} m_r (\mathbf{C}\cdot\mathbf{C}^{v-1})^{a_r-1}\right]\mathbf{F}\mathbf{C}^{v-1} - p\mathbf{F}^{-T}, \quad (3.6)$$

where we recall that $\mathbf{C} = \mathbf{F}^T\mathbf{F}$, $\mathbf{C}^v = \mathbf{F}^{vT}\mathbf{F}^v$, and p stands for the arbitrary hydrostatic pressure associated with the incompressibility constraint $\det\mathbf{F} = 1$. In turn, after some algebraic manipulation and upon recalling the identities $I_1^e = \mathbf{C}\cdot\mathbf{C}^{v\,-1}$ and $I_2^e = 1/2[(\mathbf{C}\cdot\mathbf{C}^{v\,-1})^2 - \mathbf{C}^{v\,-1}\mathbf{C}\cdot\mathbf{C}\mathbf{C}^{v\,-1}]$, the ensuing evolution equation $(2.16)_2$ can be written as

$$\dot{\mathbf{C}}^v = \frac{\sum_{r=1}^{2} 3^{1-a_r} m_r (\mathbf{C}\cdot\mathbf{C}^{v\,-1})^{a_r-1}}{\eta_K(I_1^e, I_2^e, I_1^v)} \left(\mathbf{C} - \frac{1}{3}(\mathbf{C}\cdot\mathbf{C}^{v\,-1})\mathbf{C}^v\right) \doteq \mathbf{G}(t, \mathbf{C}^v), \qquad (3.7)$$

where the function $\mathbf{G}$ of time t and $\mathbf{C}^v$ has been defined for subsequent notational convenience. We note that the stress-deformation response (3.6) depends on the internal variable $\mathbf{F}^v$ only through $\mathbf{C}^v$, which is defined implicitly by the nonlinear first-order ordinary differential equation (3.7) in terms of the applied deformation as characterized by $\mathbf{C}$. We further note that the differential equation (3.7) implies that $\det\mathbf{C}^v = \det\mathbf{F}^v = 1$, as expected from the unbounded value of the viscosity η_J in (3.3). The following additional remarks are in order:

- *Linearization.* In the limit of small deformations as $\mathbf{F} \to \mathbf{I}$ with $\det\mathbf{F} = 1$, the stress-deformation response (3.6) and evolution equation (3.7) linearize properly as they reduce asymptotically to

$$\begin{aligned} \mathbf{S} &= 2(\mu_1 + \mu_2)\mathbf{E} + 2(m_1 + m_2)(\mathbf{E} - \mathbf{E}^v) + p\mathbf{I} \\ \dot{\mathbf{E}}^v &= \frac{m_1 + m_2}{\eta_0}(\mathbf{E} - \mathbf{E}^v) \end{aligned} \qquad (3.8)$$

  to leading order, where $\mathbf{E} = 1/2(\mathbf{F} + \mathbf{F}^T - 2\mathbf{I})$ and $\mathbf{E}^v = 1/2(\mathbf{F}^v + \mathbf{F}^{vT} - 2\mathbf{I})$. Relations (3.8) are nothing more than the constitutive relation for the so-called standard solid model in classical linear viscoelasticity.

- *Numerical solution of the evolution equation (3.7).* Under conditions of finite deformation, the nonlinear evolution equation (3.7) does not admit explicit solutions. Nevertheless, being a system of six nonlinear first-order differential equations for the six components C_{11}^v, C_{22}^v, C_{33}^v, C_{12}^v, C_{13}^v, C_{23}^v, it is a simple matter to generate numerical solutions for it. For instance, a possible numerical method of solution that preserves the required condition of incompressibility $\det\mathbf{C}^v = 1$ at every time step is given by the exponential implicit first-order Euler scheme (see, e.g., [29]). For a generic time interval $[t_n, t_{n+1}]$, this scheme provides the updated value of the solution $\mathbf{C}^v_{t=t_{n+1}}$ in

terms of the solution at the previous time step $\mathbf{C}^v_{t=t_n}$ by the rule

$$\mathbf{C}^v_{t=t_{n+1}} = \exp\left[\Delta t\, \mathbf{G}(t_{n+1}, \mathbf{C}^v_{t=t_{n+1}})\mathbf{C}^{v-1}_{t=t_n+1}\right] \mathbf{C}^v_{t=t_n}, \tag{3.9}$$

where $\Delta t = t_{n+1} - t_n$. Numerical experiments — making use of the standard Newton-Rapshon scheme to solve the nonlinear algebraic equations (3.9) — for a variety of values of the material parameters and a variety of deformation histories $\mathbf{F} = \mathbf{F}(t)$ have confirmed that (3.9) is indeed a robust scheme to generate numerical solutions for (3.7). We have also found robust the explicit fifth-order Runge-Kutta scheme with extended region of stability due to Lawson [30], which is given by the rule

$$\mathbf{C}^v_{t=t_{n+1}} = \mathbf{C}^v_{t=t_n} + \frac{\Delta t}{90}(7\mathbf{k}_1 + 32\mathbf{k}_3 + 12\mathbf{k}_4 + 32\mathbf{k}_5 + 7\mathbf{k}_6) \tag{3.10}$$

with

$$\begin{aligned}
\mathbf{k}_1 &= \mathbf{G}(t_n, \mathbf{C}^v_{t_n}) \\
\mathbf{k}_2 &= \mathbf{G}(t_n + \Delta t/2, \mathbf{C}^v_{t_n} + \mathbf{k}_1\, \Delta t/2) \\
\mathbf{k}_3 &= \mathbf{G}(t_n + \Delta t/4, \mathbf{C}^v_{t_n} + (3\mathbf{k}_1 + \mathbf{k}_2)\, \Delta t/16) \\
\mathbf{k}_4 &= \mathbf{G}(t_n + \Delta t/2, \mathbf{C}^v_{t_n} + \mathbf{k}_3\, \Delta t/2) \\
\mathbf{k}_5 &= \mathbf{G}(t_n + 3\Delta t/4, \mathbf{C}^v_{t_n} + 3(-\mathbf{k}_2 + 2\mathbf{k}_3 + 3\mathbf{k}_4)\, \Delta t/16) \\
\mathbf{k}_6 &= \mathbf{G}(t_n + \Delta t, \mathbf{C}^v_{t_n} + (\mathbf{k}_1 + 4\mathbf{k}_2 + 6\mathbf{k}_3 - 12\mathbf{k}_4 + 8\mathbf{k}_5)\, \Delta t/7)
\end{aligned} \tag{3.11}$$

where $\Delta t = t_{n+1} - t_n$. Being explicit, the scheme (3.10)–(3.11) is easier to implement than (3.9) and, although it requires much smaller time increments Δt, also less computationally costly.

- *Determination of the material parameters from experimental data.* The constitutive relation (3.6)–(3.7) contains fourteen material parameters: four (μ_1, μ_2, α_1, α_2) describing the non-Gaussian elasticity at states of thermodynamic equilibrium, four (m_1, m_2, a_1, a_2) describing the additional non-Gaussian elasticity of non-equilibrium states, and six (η_0, η_∞, β_1, β_2, K_1, K_2) describing the viscous dissipation that stems from the reptational motion of the underlying polymer chains. These parameters can be determined by simply fitting (e.g., by means of least squares) the model simultaneously

to a set of uniaxial relaxation data and a set of uniaxial tension/compression data at constant deformation rate. Alternatively, they can be determined by fitting simultaneously two sets of uniaxial tension/compression data at two sufficiently different constant deformation rates. While fitting more complex sets of data (when available) may lead to improved predictive capabilities, the values of the parameters determined by these simple procedures have been tested to generate models with good predictive capabilities for a variety of elastomers, as illustrated in the next subsection.

- *Homogenization problems.* Because of its derivation from two thermodynamic potentials that are functions of the deformation gradient tensor $\mathbf{F}$ and an internal variable $\mathbf{F}^v$ grounded in the undeformed configuration, the constitutive relation (3.6)–(3.7) is well suited for use in boundary-value problems, particularly in homogenization problems [31] such as for instance those that arise in the modelling of filled elastomers [32] and in cavitation phenomena in soft adhesives [33, 34].

CHAPTER 4

SAMPLE COMPARISONS WITH EXPERIMENTS

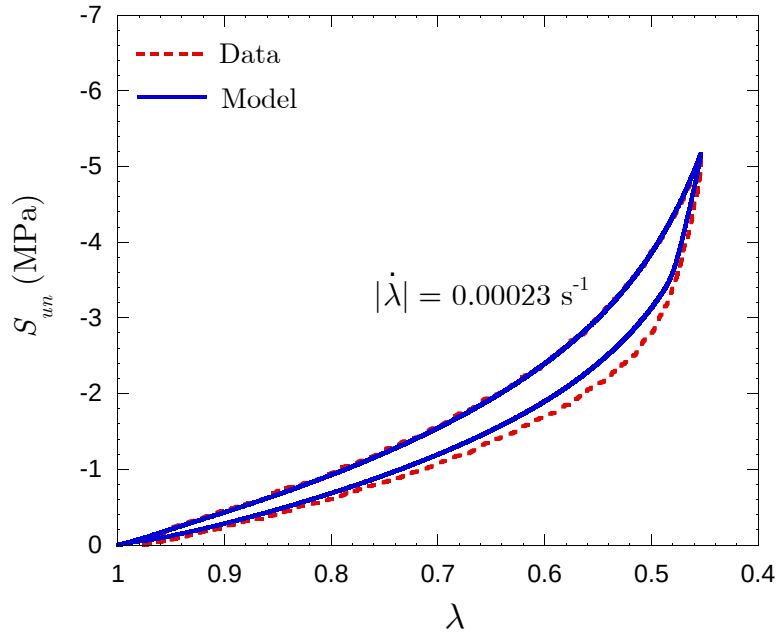
We conclude by illustrating the descriptive and predictive capabilities of the proposed model through sample comparisons with experimental data available from the literature for two commercially significant elastomers, namely, the data of Bergström and Boyce [7] for Nitrile rubber and the data of Hossain et al. [35] for the acrylate elastomer VHB 4910 from 3M.

Nitrile rubber The experimental data of Bergström and Boyce [7] for Nitrile rubber pertain to uniaxial compression loading/unloading tests, with $\mathbf{F} = 1/\sqrt{\lambda(t)}(\mathbf{e}_1 \otimes \mathbf{e}_1 + \mathbf{e}_2 \otimes \mathbf{e}_2) + \lambda(t)\mathbf{e}_3 \otimes \mathbf{e}_3$ and $\mathbf{S} = S_{un}\mathbf{e}_3 \otimes \mathbf{e}_3$, conducted at four different constant stretch rates $|\dot{\lambda}| = 0.00023, 0.001, 0.01, 0.1\ \mathrm{s}^{-1}$. As relaxation experiments were not reported, we simultaneously fitted (by means of least squares) the constitutive model (3.6)–(3.7) to the data for the two stretch rates $|\dot{\lambda}| = 0.00023$ and $0.01\ \mathrm{s}^{-1}$ in order to determine the fourteen material parameters of the model; fitting the data for two other stretch rates was checked to lead to similar results. Table 1 displays the resulting values for the parameters.

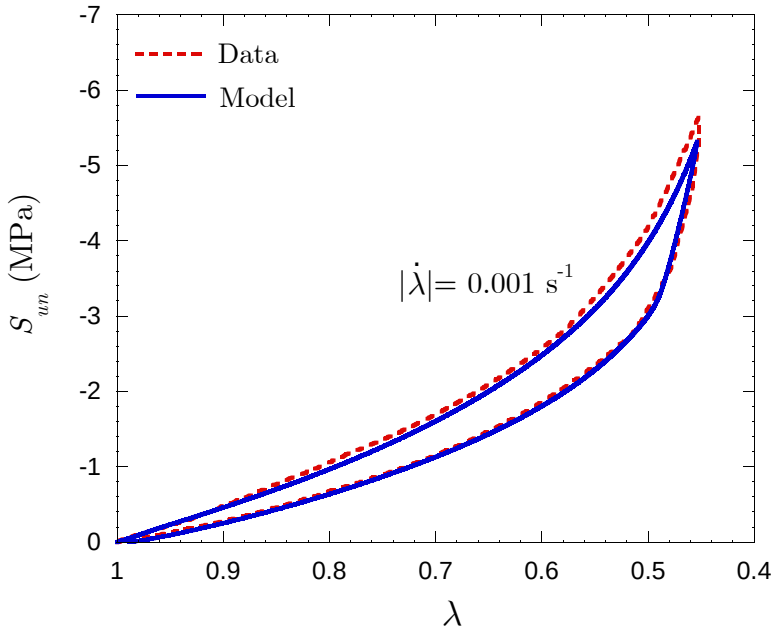
Table 4.1: Material parameters for Nitrile rubber

$\mu_1 = 1.08\,\mathrm{MPa}$	$\mu_2 = 0.017\,\mathrm{MPa}$	$\alpha_1 = 0.26$	$\alpha_2 = 7.68$
$m_1 = 1.57\,\mathrm{MPa}$	$m_2 = 0.59\,\mathrm{MPa}$	$a_1 = -10$	$a_2 = 7.53$
$\eta_0 = 2.11\,\mathrm{MPa}\cdot\mathrm{s}$	$\eta_\infty = 0.1\,\mathrm{MPa}\cdot\mathrm{s}$	$\beta_1 = 3$	$\beta_2 = 1.929$
$K_1 = 442\,\mathrm{MPa}\cdot\mathrm{s}$	$K_2 = 1289.49\,\mathrm{MPa}^{-2}$		

Figure 4.1 displays plots of the stress-stretch response of the Nitrile rubber for all four stretch rates $|\dot{\lambda}| = 0.00023, 0.001, 0.01, 0.1\ \mathrm{s}^{-1}$. The dashed lines in the plots correspond to the experimental data, while the solid lines correspond to results from the proposed model with the material parameters of Table 4.1. Figures 4.1(a) and (c) show that the data for the two stretch rates that were utilized in the determination of the material parameters, $|\dot{\lambda}| = 0.00023$ and $0.01\ \mathrm{s}^{-1}$, are well described by the model. Figures 4.1(b) and (d) show further that the data

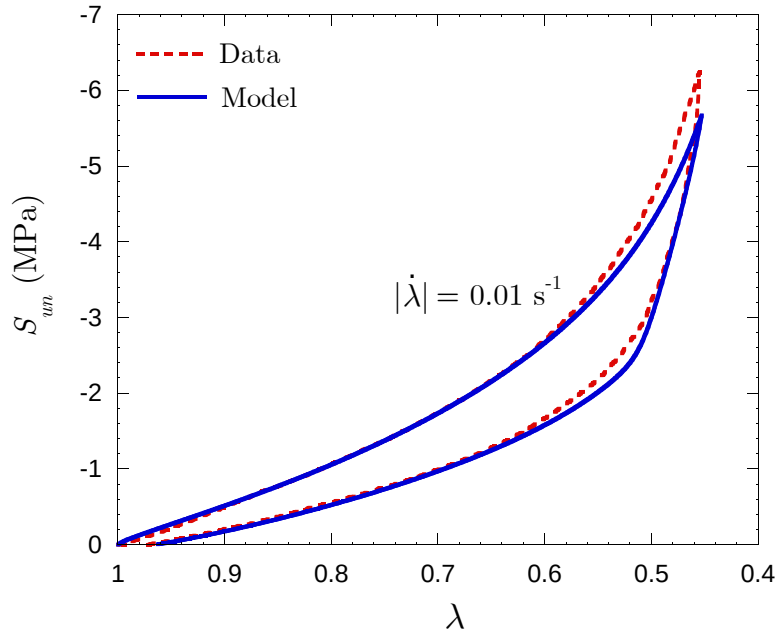


(a)

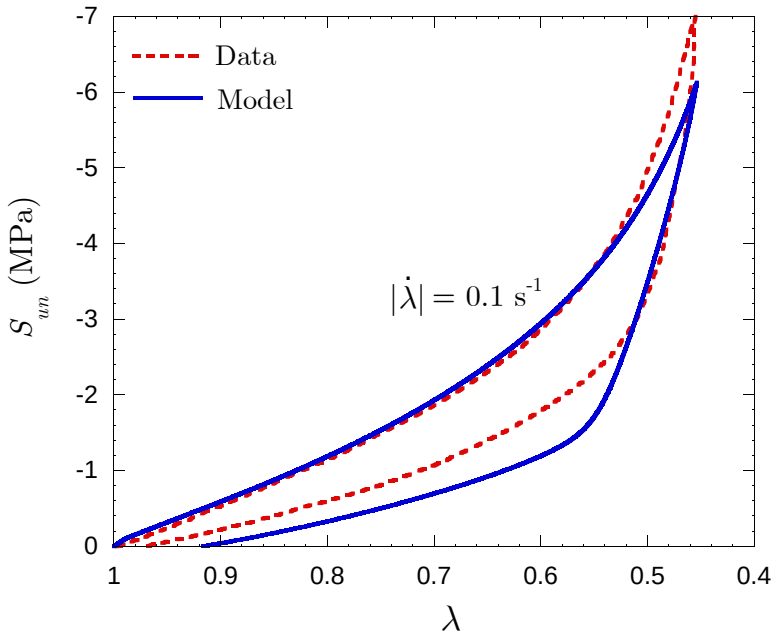


(b)

Figure 4.1: The proposed model (3.6)–(3.7), with the material parameters of Table 1, compared with the experimental data of Bergström and Boyce [7] for Nitrile rubber subjected to uniaxial compression loading/unloading at constant stretch rates of: (a) $|\dot{\lambda}| = 0.00023\ \mathrm{s}^{-1}$, (b) $|\dot{\lambda}| = 0.001\ \mathrm{s}^{-1}$, (c) $|\dot{\lambda}| = 0.01\ \mathrm{s}^{-1}$, (d) $|\dot{\lambda}| = 0.1\ \mathrm{s}^{-1}$.



(c)



(d)

Figure 4.1: (cont.)

for the other two stretch rates, $|\dot{\lambda}| = 0.001$ and $0.1\ \mathrm{s}^{-1}$, are well *predicted* by the model.

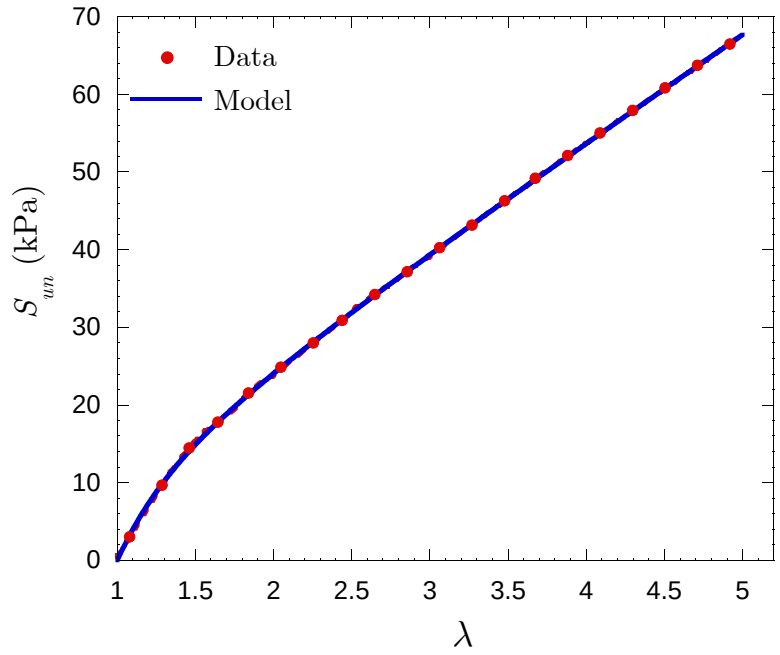
The acrylate elastomer VHB 4910 The experimental data of Hossain et al. [35] comprise uniaxial tension loading/unloading tests, with $\mathbf{F} = 1/\sqrt{\lambda(t)}(\mathbf{e}_1 \otimes \mathbf{e}_1 + \mathbf{e}_2 \otimes \mathbf{e}_2) + \lambda(t)\mathbf{e}_3 \otimes \mathbf{e}_3$ and $\mathbf{S} = S_{un}\mathbf{e}_3 \otimes \mathbf{e}_3$, conducted at three different constant stretch rates $|\dot{\lambda}| = 0.01, 0.03, 0.05\ \mathrm{s}^{-1}$, as well as single- and multi-step relaxation tests also in uniaxial tension.[1] In this case, we determined the material parameters of the model by simultaneously fitting three sets of data: the equilibrium states obtained from the multi-step relaxation test and two uniaxial tension loading/unloading tests at constant stretch rates $|\dot{\lambda}| = 0.01, 0.05\ \mathrm{s}^{-1}$. The resulting values for the parameters are given in Table 2.

Table 4.2: Material parameters for VHB 4910

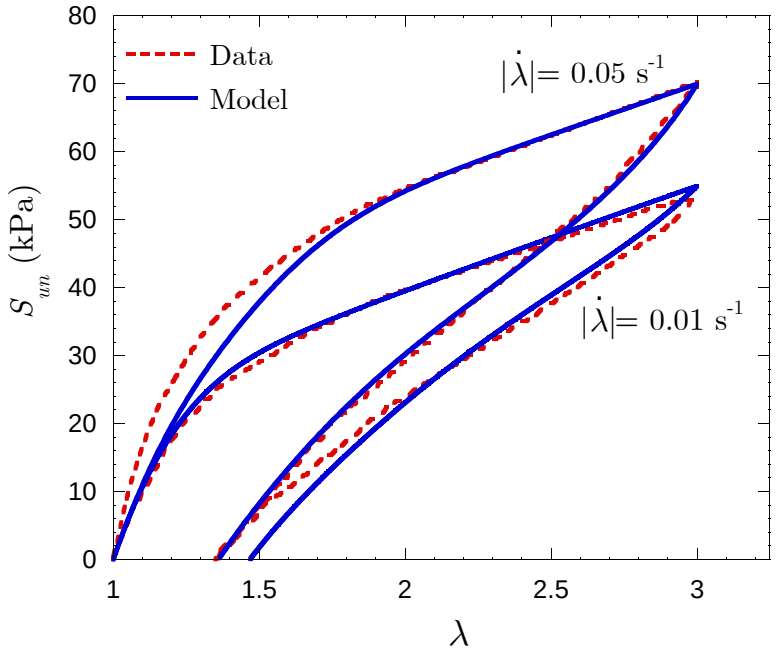
$\mu_1 = 13.54\,\mathrm{kPa}$	$\mu_2 = 1.08\,\mathrm{kPa}$	$\alpha_1 = 1.00$	$\alpha_2 = -2.474$
$m_1 = 5.42\,\mathrm{kPa}$	$m_2 = 20.78\,\mathrm{kPa}$	$a_1 = -10$	$a_2 = 1.948$
$\eta_0 = 7014\,\mathrm{kPa}\cdot\mathrm{s}$	$\eta_\infty = 0.1\,\mathrm{kPa}\cdot\mathrm{s}$	$\beta_1 = 1.852$	$\beta_2 = 0.26$
$K_1 = 3507\,\mathrm{kPa}\cdot\mathrm{s}$	$K_2 = 1\,\mathrm{kPa}^{-2}$		

Figures 4.2(a) and (b) show comparisons between the experimental data (dashed lines) that were utilized in the determination of the material parameters and the model (solid lines). Figures 4.2(c) and (d) show further comparisons between experiments and corresponding results from the model for a uniaxial tension loading/unloading test at constant stretch rate $|\dot{\lambda}| = 0.03\ \mathrm{s}^{-1}$ and for two single-step relaxation tests with stretches held at $\lambda = 2$ and 4.5. Similar to the case of Nitrile rubber, the model is seen to describe and predict the response of the acrylate elastomer VHB 4910 reasonably well.

[1] As opposed to the data for Nitrile rubber considered above for which the Mullins effect was reported to have been removed, it is unknown whether the data for the acrylate elastomer VHB 4910 considered here was obtained after removing the Mullins effect.

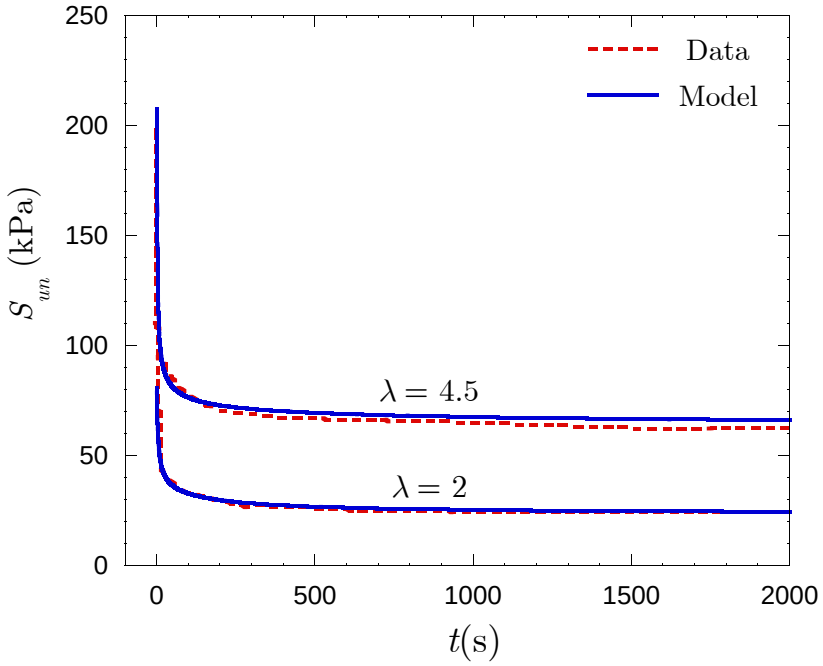


(a)

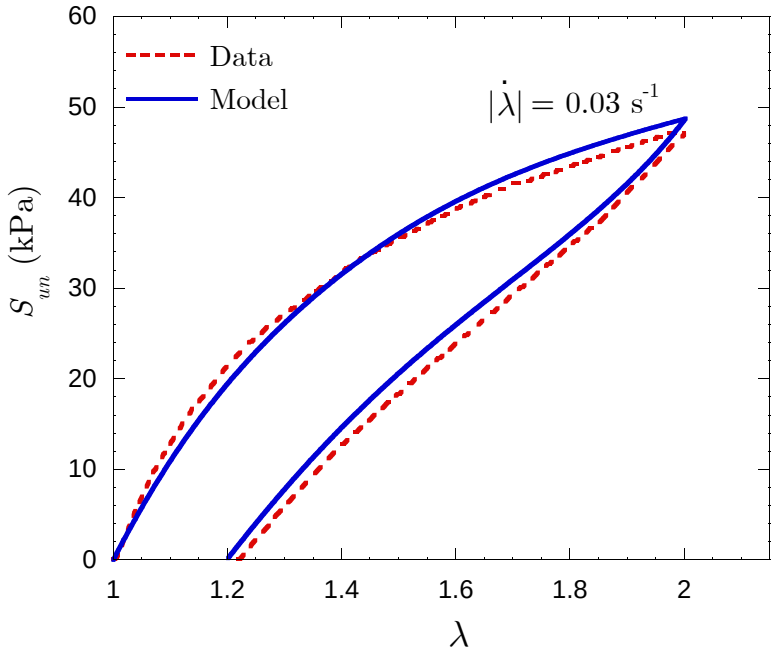


(b)

Figure 4.2: The proposed model (3.6)–(3.7), with the material parameters of Table 2, compared with the experimental data of Hossain et al. [35] for VHB 4910: (a) equilibrium stress-stretch states from a multi-step relaxation test, (b)–(c) uniaxial tension loading/unloading tests at constant stretch rates $|\dot{\lambda}| = 0.01, 0.03, 0.05$ s^{-1}, (d) two single-step relaxation tests with stretches held at $\lambda = 2$ and 4.5.



(c)



(d)

Figure 4.2: (cont.)

REFERENCES

[1] A.E. Green, R.S. Rivlin, The mechanics of non-linear materials with memory, Arch. Rational Mech. Anal. 1 (1957) 1–21.

[2] A.C. Pipkin, T.G. Rogers, A nonlinear integral representation for viscoelastic behavior, J. Mech. Phys. Solids 16 (1968) 59–72.

[3] F.J. Lockett, Nonlinear Viscoelastic Solids, Academic Press, London, New York, 1972.

[4] F. Sidoroff, Un modèle viscoélastique non linéaire avec configuration intermédiaire, Journal de Mécanique 13 (1974) 679–713.

[5] P. Le Tallec, C. Rahier, A. Kaiss, Three-dimensional incompressible viscoelasticity in large strains: formulation and numerical approximation, Computer Methods in Applied Mechanics and Engineering 109 (1993) 233–258.

[6] S. Reese, S. Govindjee, A theory of finite viscoelasticity and numerical aspects, International Journal of Solids and Structures 35 (1998) 3455–3482.

[7] J.S. Bergström, M.C. Boyce, Constitutive modeling of the large strain time-dependent behavior of elastomers, Journal of the Mechanics and Physics of Solids 46 (1998) 931–954.

[8] C. Miehe, S. Göktepe, A micro–macro approach to rubber-like materials. Part II: The micro-sphere model of finite rubber viscoelasticity, Journal of the Mechanics and Physics of Solids 53 (2005) 2231–2258.

[9] C. Linder, M. Tkachuk, C. Miehe, A micromechanically motivated diffusion-based transient network model and its incorporation into finite rubber viscoelasticity, Journal of the Mechanics and Physics of Solids 59 (2011) 2134–2156.

[10] B.D. Coleman, M.E. Gurtin, Thermodynamics with internal state variables, Journal of Chemical Physics 47 (1967) 597–613.

[11] H. Ziegler, An attempt to generalize Onsager's principle, and its significance for rheological problems, Z. Angew. Math. Phys. 9b (1958) 748–763.

[12] B. Halphen, Q.S. Nguyen, Sur les matériaux standard généralisés, Journal de Mécanique 14 (1975) 39–63.

[13] P. Germain, Q.S. Nguyen, P. Suquet, Continuum thermodynamics, Journal of Applied Mechanics 50 (1983) 1010–1020.

[14] H. Ziegler, C. Wehrli, The derivation of constitutive relations from the free energy and the dissipation function, Advances in Applied Mechanics 25 (1987) 183–238.

[15] K. Hackl, Generalized standard media and variational principles in classical and finite strain elastoplasticity, Journal of the Mechanics and Physics of Solids 45 (1997) 667–688.

[16] B. Bourdin, G.A. Francfort , J.-J. Marigo, The variational approach to fracture, Journal of Elasticity 91 (2008) 5–148.

[17] A. Mielke, A mathematical framework for standard generalized materials in the rate-independent case, In R. Helmig, A. Mielke, B. Wohlmuth (editors), Multifield problems in Fluid and Solid Mechanics. Series Lecture Notes in Applied and Computational Mechanics, 28 (2006) 399–428.

[18] L. Laiarinandrasana, R. Piques, A. Robisson, Visco-hyperelastic model with internal state variable coupled with discontinuous damage concept under total Lagrangian formulation, Int. J. Plast. 19 (2003) 977–1000.

[19] J.M. Martinez, A. Boukamel, S. Meo, S. Lejeunes, Statistical approach for a hyper-visco-plastic model for filled rubber: experimental characterization and numerical modeling, Eur. J. Mech. A, Solids 30 (2011) 1028–1039.

[20] E.M. Arruda, M.C. Boyce, A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials, J. Mech. Phys. Solids 41 (1993) 389–412.

[21] O. Lopez-Pamies, A new I_1–based hyperelastic model for rubber elastic materials, Comptes Rendus Mecanique 338 (2010) 3–11.

[22] S.F. Edwards, Statistical mechanics with topological constraints. I. Proc. Phys. Soc. 91 (1967), 513–519.

[23] P.G. de Gennes, Reptation of a polymer chain in the presence of fixed obstacles, J. Chem. Phys. 55 (1971) 572–579.

[24] M. Doi, S.F. Edwards, The Theory of Polymer Dynamics, Oxford University Press, New York, 1998.

[25] A.N. Gent, Relaxation processes in vulcanized rubber. I. Relation among stress relaxation, creep, recovery, and hysteresis, J. Appl. Polym. Sci. 6 (1962a) 433–441.

[26] A.N. Gent, Relaxation processes in vulcanized rubber. II. Secondary relaxation due to network breakdown, J. Appl. Polym. Sci. 6 (1962b) 442–448.

[27] A.S. Khan, O. Lopez-Pamies, 2002. Time and temperature dependent response and relaxation of a soft polymer. Int. J. Plasticity 18 (2002) 1359–1372.

[28] A.F.M.S. Amin, A. Lion, S. Sekita, Y. Okui, Nonlinear dependence of viscosity in modeling the rate-dependent response of natural and high damping rubbers in compression and shear: Experimental identification and numerical verification, International Journal of Plasticity 22 (2006) 1610–1657.

[29] J.C. Simo, Algorithms for static and dynamic multiplicative plasticity that preserve the classical return mapping schemes of the infinitesimal theory, Computer Methods in Applied Mechanics and Engineering 99 (1992) 61–112.

[30] J.D. Lawson, An order five Runge-Kutta process with extended region of stability, SIAM Journal on Numerical Analysis 3 (1966) 593–597.

[31] N. Lahellec, P. Suquet, 2007. On the effective behavior of nonlinear inelastic composites: I. Incremental variational principles. J. Mech. Phys. Solids 55 (2007) 1932–1963.

[32] T. Goudarzi, D.W. Spring, G.H. Paulino, O. Lopez-Pamies, Filled elastomers: A theory of filler reinforcement based on hydrodynamic and interphasial effects. Journal of the Mechanics and Physics of Solids 80 (2015) 37–67.

[33] C. Creton, J. Hooker, K.R. Shull, Bulk and interfacial contributions to the debonding mechanisms of soft adhesives: Extension to large strains, Langmuir 17 (2001) 4948–4954.

[34] O. Lopez-Pamies, M.I. Idiart, T. Nakamura, Cavitation in elastomeric solids: I — A defect-growth theory. Journal of the Mechanics and Physics of Solids 59 (2011) 1464–1487.

[35] M. Hossain, D.K. Vu, P. Steinmann, Experimental study and numerical modelling of VHB 4910 polymer, Computational Materials Science 59 (2012) 65–74.